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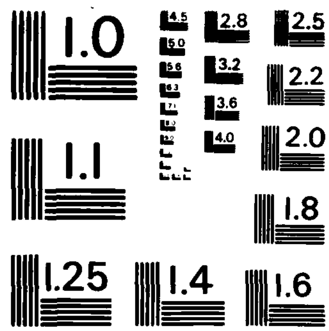

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LOW COST ACETYLENE TERMINATED POLYMERS

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February 1984

Final Report for Period 27 September 1982 to 30 September 1983

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A three step procedure for the synthesis of acetylene terminated polymers was studied. The meta- and para- ATB systems, made from Bis Phenol A, were used to develop a process which would be amenable to large scale production. Several changes in the work-up of the reactions were made to reduce the use of carcinogenic solvents and to eliminate costly and unwieldy chromatography columns. The use of toluene as a solvent permitted efficient removal of palladium and copper at significantly lower cost. Products and major by-products in the three steps were characterized by analytical techniques including HPLC and NMR,

FOREWORD

This report entitled "Low Cost Acetylene Terminated Polymers", was prepared by Raylo Chemicals Limited and covers work carried out under Contract No. F33615-82-C-5051, project number 2303Q318, which was awarded through the Canadian Commercial Corporation as their Contract No. 24SR.70C3-82-R-5051. It was administered under the direction of Air Force Wright Aeronautical Laboratories, Materials Laboratory, Air Force Systems Command, United States Air Force, Wright-Patterson AFB, Ohio 45433. Initially, Dr. F.L. Hedberg was the Project Engineer but he was later replaced by Lt. P.M. Lindley.

This report describes work conducted from October 1982 to October 1983. The work described in this report was conducted at Raylo Chemicals Limited's laboratories located in Edmonton, Alberta, Canada by Dr. J.F. Prescott, Dr. R. Ippolito and S.P. Lee.

TABLE OF CONTENTS

Table of Contents .. continued

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION

The first part of the work, representing four months of effort, was directed towards the examination of the effects of changes of the stoichiometric ratio of collidine, meta- or para- dibromobenzene and bisphenol-A on the monomer to oligomer ratio in the Ullman ether synthesis. The second part, representing eight months of effort, was directed to the synthesis, isolation, characterization and scale-up of the synthesis of bis-(4,4'-(3-bromophenoxy)phenyl)dimethylmethane, bis-(4,4'-(3-(3-hydroxy-3-methylbutynl)phenoxy)phenyl)dimethylmethane and bis-(4,4'-(3-ethynylphenoxy)phenyl)dimethylmethane and the para-analogues. We have completed their scale-up syntheses and developed a process suitable for pilot plant scale manufacture of these products.

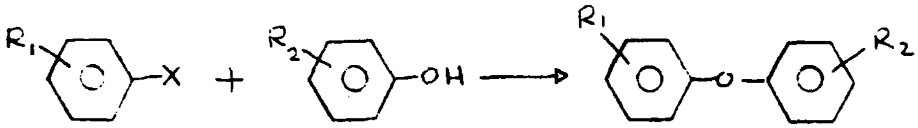
SECTION II

RESULTS AND DISCUSSION

1. Ullman Synthesis of bis-(4,4'-(3-bromophenoxy)phenyl)dimethyl methane (m-BTB) and bis-(4,4'-(4-bromophenoxy)phenyl)dimethyl methane (p-BTB)

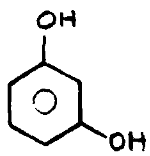
a. Background:

The Ullman ether synthesis has been widely used in the synthesis of a variety of aryl ethers [1]. Most Ullman aryl ether syntheses, however, involved monohalogenated benzene or its derivatives (1) and phenol or substituted phenols (2) to give monoethers (3) [2].



1 2 3

The reaction between dihalobenzenes and dihydroxybenzenes such as resorcinol (4) or bisphenol-A (5) to give a mixture of monomeric and polymeric ethers (6 & 7) received little attention until the potential application of polyaryl ethers as polymer resins was reported [3].



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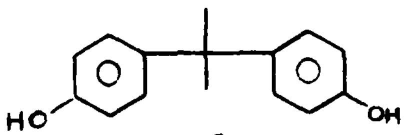

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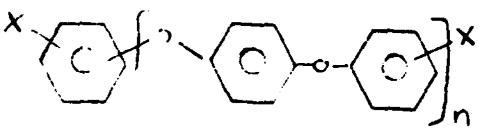

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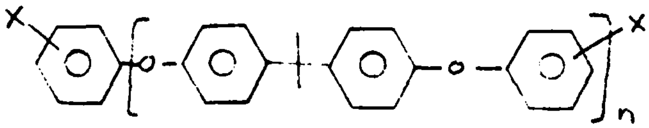
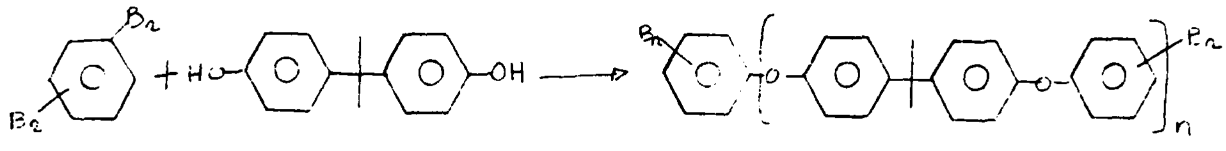
X = Cl, Br   n = 1 2, 3,



7

Recent studies by Hedberg and Lindley of the Ullman ether synthesis using meta- and para-dibromobenzene with bisphenol-A showed that the ratio of monomer to oligomer varied as the mole ratio of dibromobenzene to bisphenol-A was changed [4].



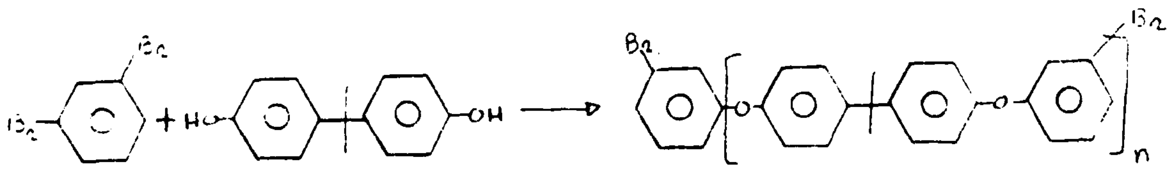
Br = m or p   5   8 = m   9 = p

n = 1, 2, 3

A stoichiometric ratio of 2:1 of m-dibromobenzene to bisphenol-A gave m-BTB containing 20% monomer and 80% oligomer. Ratios of 20:1, 10:1 and 4:1 gave products having monomer to oligomer ratios of 94:6, 89:11, and 60:40 respectively. Only one stoichiometric ratio was reported for p-dibromobenzene and bisphenol-A of 40:60. Although collidine was used as a solvent in the Ullman ether synthesis of BTB its effect on the monomer to oligomer ratio was not reported.

b. The effect of the mole ratio of collidine to bisphenol-A:

Ullman ether syntheses were carried out with a fixed mole ratio of m-dibromobenzene to bisphenol-A (10:1) using three different mole ratios of collidine to bisphenol-A and the monomer to oligomer ratio of the m-BTB product (8) measured (Table 1).



8

n = 1, 2, 3.

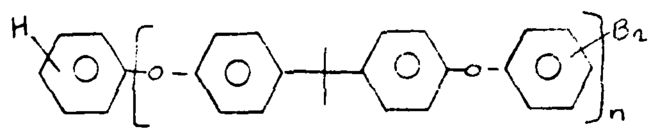
Mole ratios of collidine to bisphenol-A of 10:1 gave product with a monomer to oligomer ratio of 62:38. Mole ratios of 6:1 and 3:1 gave products with monomer to oligomer ratios of 77:33 and 73:27 respectively. At the lower mole ratios, collidine had little effect on the composition of the product. At the highest mole ratio tested, collidine increased the degree of polymerization which may be partly due to the decreased concentration of m-dibromobenzene in the reaction mixture and partly to the increased activity of the bisphenol-A in the large excess of base.

c. The effect of the mole ratio of dibromobenzene to bisphenol-A

(1) m-Dibromobenzene

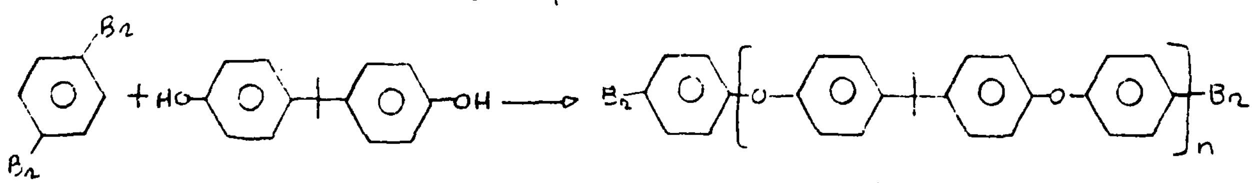
Three lots of m-BTB were prepared using a fixed ratio (10:1) of collidine to bisphenol-A but with different mole ratios of m-dibromobenzene to bisphenol-A and the monomer to oligomer ratios of the products measured (Table 2). A mole ratio of 2:1 is the stoichiometric ratio for the synthesis of monomer but gave only 20% monomer and 80% oligomer in the m-BTB produced. Increasing the mole ratio of m-dibromobenzene from 2:1 to 10:1 raised the monomer content of the products from 20% to 85%.

At any of the ratios of m-dibromobenzene to bisphenol-A less than 10:1, monobrominated products could be detected as satellite spots with Rf values slightly lower than those of the main products on tlc. The monobromo compounds (17) were isolated and characterized up to n=3.



17a = meta n = 1, 2, 3.

17b = para



9 n = 1, 2, 3.

(2) p-Dibromobenzene

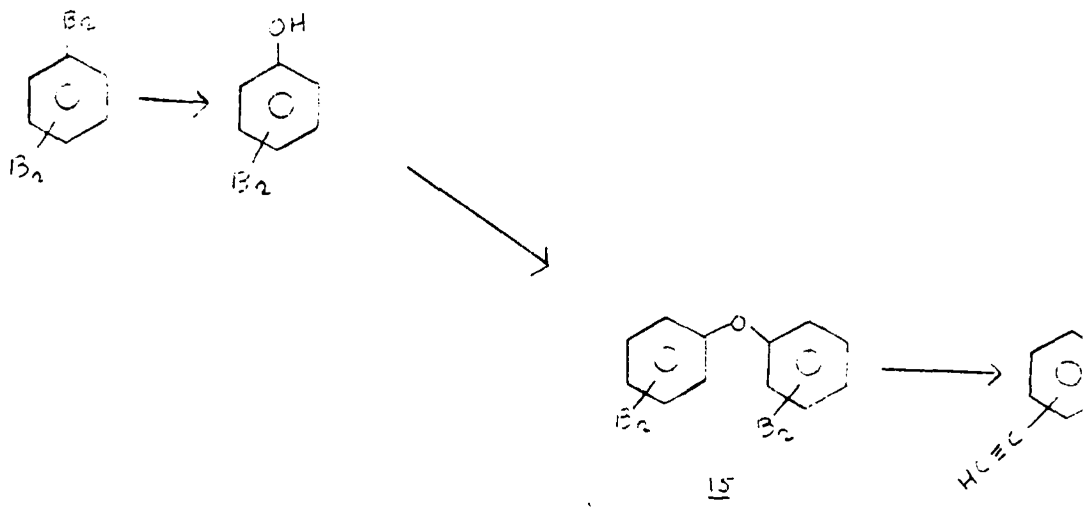
Three lots of p-BTB (9) were prepared using a fixed ratio (6:1) of collidine to bisphenol-A using different mole ratios of p-dibromobenzene to bisphenol-A (Table 3). A 2:1 mole ratio is stoichiometric for the production of monomer but gave 55% monomer and

45% oligomer. Increasing the mole ratio of p-dibromobenzene to 3 4:1 raised the monomer contents of the products to 60% an respectively.

Large scale preparation of p-BTB (9) were only made mole ratio of p-dibromobenzene to bisphenol-A of 2:1 an corresponding monobromo compounds were always present in the pr Only the monomeric material was isolated and identified.

d. The effect of water

During the course of the reaction, a small amount of wa formed and causes violent bumping of the reaction mixture. Unle water [illegible] removed it is difficult to bring the reaction temperatu to the desired 170°C. Installation of a Dean and Stark trap these problems. Traces of water could cause some partial hydroly dibromobenzene to form a little bromophenol. Condensation of bromophenol with dibromobenzene would give the bromophenyl ether which could not be separated from the desired products. bromophenyl ether then carries through the synthesis to giv ethynyl derivative (16). In all the m-BTB preparations done afte introduction of the Dean and Stark trap the quantity of the brom ether formed was reduced to the extent that it was no l detectable.



15

e. Analysis:

The m-BTB and p-BTB reaction products were analyzed by hplc using a RP OD18 column (Waters Associates) and aqueous tetrahydrofuran as the mobile phase. Good resolutions were obtained with a solvent mixture containing 28% water and 72% tetrahydrofuran (Fig. 1 and 2). Column chromatography was also used to measure the monomer to oligomer ratio. The results obtained by hplc are compared with those obtained by column chromatography in Table 4. The correspondence was extremely good.

f. Conclusions:

Clearly m-dibromobenzene is more reactive than p-dibromobenzene. This finding is not surprising as unactivated meta substituted halobenzenes are known to be more reactive than their para analogues in aromatic nuclear substitution reactions such as the Ullman ether synthesis [5]. The m-BTB products would also be expected to be more reactive than the p-BTB products and this is confirmed by the greater amount of polymeric products made in the m-BTB reactions.

2. Isolation and Characterization of the Reaction Products

a. Bromo terminated products:

The components of m-BTB and of p-BTB were isolated by column chromatography on silica gel using a mixture of toluene and hexane as eluant. A loading of 1 part of crude mixture per 25 parts of silica gel was satisfactory.

The m-BTB components were isolated from a sample prepared by reacting m-dibromobenzene and bisphenol-A in a mole ratio of 3:1 so as to obtain the oligomers in substantial quantities. The p-BTB components were obtained from reactions on p-dibromobenzene and bisphenol-A in a mole ratio of 2:1.

(1) m-Bromo terminated compounds

m-BTB monomer

H'nmr spectrum

singlet	d 1.70	BPA methyl
multiplet	d 6.8-7.3	aromatic

High resolution mass spectrum

molecular ion	537.9981	$C_{27}H_{22}Br_2O_2$

The structure (8; n=1) is consistent with these results.

m-BTB dimer

H'nmr spectrum

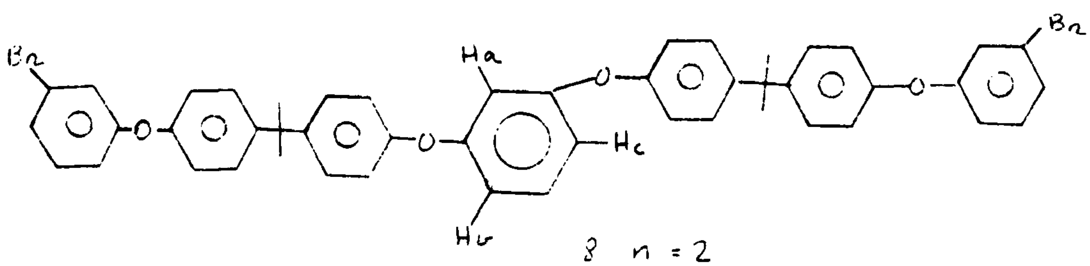
singlet	d 1.70	BPA methyl
tr dbl	d 6.7	aromatic - see below
multiplet	d 6.8-7.3	aromatic

This 3-proton triplet of doublets was assigned to the protons (Ha, Hb, and Hc), ortho- to the ether oxygens in the structure below. The assignment was based on the reporting of similar shifts in the spectrum of m-methoxyanisole [6]. These resonances are typical of all the meta-oligomers.

Low resolution mass spectrum

molecular ion	840.	$C_{48}H_{40}Br_2O_4$

The structure, (8; n=2) is consistent with these results.



8 n = 2

m-BTB trimer

H'nmr spectrum

singlet	d 1.70	BPA methyl
tr dbl	d 6.8-7.3	aromatic meta subst
multiplet	d 6.8-7.3	aromatic

High resolution mass spectrum

unsatisfactory spectrum

The structure (8; n=3) is consistent with the nmr spectrum.

(2) p-Bromo terminated products

m-BTB monomer

H'nmr spectrum

singlet	d 1.65	BPA methyl
multiplet	d 6.0-7.3	aromatic

High resolution mass spectrum

molecular ion	537.9950	$C_{27}H_{22}Br_2O_2$

The structure, (9; n=1), is consistent with these results.

p-BTB dimer

H'nmr spectrum

singlet	d 1.68	BPA methyl
multiplet	d 6.8-7.5	aromatic

Low resolution mass spectrum

molecular ion	840	$C_{48}H_{40}Br_2O_4$

The structure, (9; n=2), is consistent with the nmr spectrum.

p-BTB trimer

This component was not isolated in sufficient purity for characterization.

p-MonobromoTB monomer

H'nmr spectrum

singlet	d 1.67	BPA methyl
multiplet	d 6.8-7.5	aromatic

High resolution mass spectrum

molecular ion	459.0915	$C_{27}H_{23}BrO_2$

Bromine analysis confirmed the presence of only one bromine atom in the molecule.

The structure (17, n = 1) is consistent with these results.

p-MonobromoTB trimer

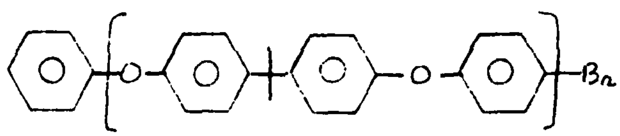
H'nmr spectrum

singlet	d 1.68	BPA methyl
multiplet	d 6.8-7.5	aromatic

Low resolution mass spectrum

molecular ion	1042.	$C_{69}H_{59}BrO_6$

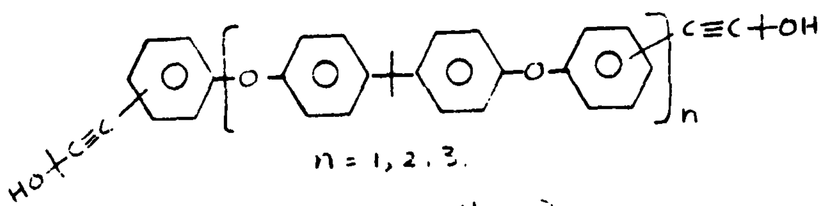
The structure, (17, n = 3), is consistent with these results.



17b n = 1, 2, 3.

b. Hydroxymethylbutynyl compounds (HTB):

These materials are the meta- and para-series monomer and oligomer mixtures of bis-(4,4'-(3-hydroxy-3-methylbutynylphenoxy)-phenyl)dimethylmethane (m-HTB (10) and p-HTB (11)).



n = 1, 2, 3.

10 = meta 11 = para

The components of m-HTB and of p-HTB were isolated by column chromatography on silica gel using mixtures of acetone and toluene as eluant. A column loading of 1:25 of sample:silica gel was found to be satisfactory. The order of elution of the hydroxy-compounds was different from the order of elution of the corresponding non polar compounds.

(1) m-HTB terminated products

m-HTB monomer

White crystalline solid

H'nmr spectrum

singlet	d 1.57	hydroxypentynyl methyl
singlet	d 1.67	BPA methyl
multiplet	d 7.1 c	aromatic

integration ratio singlet (1.57):singlet (1.67) = 2:1

High resolution mass spectrum

molecular ion 544.1357 $C_{36}H_{36}O_4$

The structure, (10; n = 1), is consistent with these results.

m-HTB dimer

H'nmr spectrum

singlet	d 1.57	hydroxypentynyl methyl
singlet	d 1.70	BPA methyl
tr dbl	d 6.6-6.8	aromatic meta subst.
multiplet	d 6.8-7.3	aromatic

integration ratio singlet (1.57):singlet (1.70) = 1:1

High resolution mass spectrum

unsatisfactory spectrum

The structure, (10; n = 2), is consistent with the nmr spectrum.

m-Hydroxyisopentnylphenyl ether

White crystalline solid

H'nmr spectrum

singlet	d 1.57	hydroxypentynyl methyl
multiplet	d 6.9-7.3	aromatic

integration ratio singlet:multiplet = 3:2

High resolution mass spectrum

molecular ion 334.1567 $C_{22}H_{22}O_3$

The title structure (12) is consistent with these results.

m-Di-3-hydroxyisopentynylbenzene

White crystalline solid

H'nmr spectrum

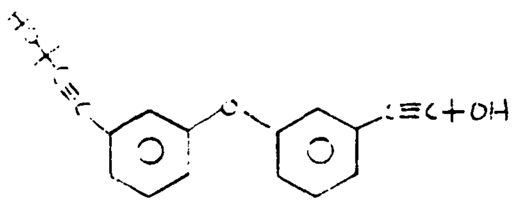
singlet	d 1.57	hydroxypentynyl methyl
multiplet	d 7.3-7.5	aromatic

integration ratio singlet:multiplet = 3:1

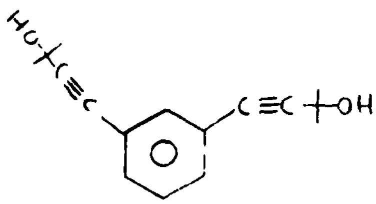
High resolution mass spectrum

molecular ion 242.1301 $C_{16}H_{18}O_2$

The title structure (13) is consistent with these results.



12



13

(2) p-HTB compounds

p-HTB monomer

H'nmr spectrum

singlet	d 1.58	hydroxypentynyl methyl
singlet	d 1.69	BPA methyl
multiplet	d 7.1 c	aromatic

integration ratio singlet (1.58):singlet (1.69) = 2:1

High resolution mass spectrum

unsatisfactory spectrum

p-HTB dimer

H'nmr spectrum

singlet	d 1.58	hydroxypentynyl methyl
singlet	d 1.69	BPA methyl
multiplet	d 7.1 c	aromatic

integration ratio singlet (1.58):singlet (1.69) = 1:1

Low resolution mass spectrum

molecular ion 846. $C_{53}H_{54}O_6$

The structure, (9; n = 2), is consistent with the nmr spectrum.

By-product

H'nmr spectrum

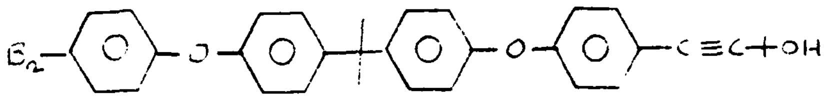
singlet	d 1.57	hydroxypentynyl methyl
singlet	d 1.68	BPA methyl
multiplet	d 6.8-7.5	aromatic

integration ratio singlet (1.57):singlet (1.68) = 1:1

High resolution mass spectrum

molecular ion 542.1291 $C_{32}H_{29}BrO_3$

The compound is clearly monobromo terminated and mono-hydroxyisopentynyl terminated and the structure (24) given below is consistent with these results.

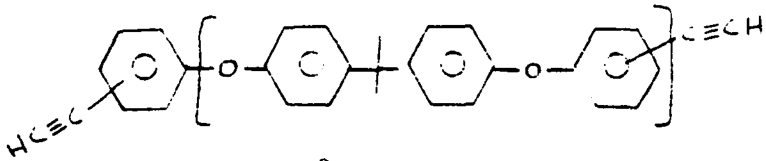


24

c. Ethynyl compounds

These materials are the meta- and para-series of monomer and oligomer mixtures of bis-(4,4'-(ethynylphenoxy)phenyl)dimethylmethane (m-ATB (18) and p-ATB (19)).

The components of m-ATB and of p-ATB were isolated by column chromatography on silica gel using a mixture of toluene and hexane as eluant. A column loading of 1:20 of sample to silica gel was found to be satisfactory for these separations.



18 = m-ATB

19 = p-ATB

(1) m-Ethynyl products

m-ATB monomer

H'nmr spectrum

singlet	d 1.7	BPA methyl
singlet	d 2.1	ethynyl
multiplet	d 7.0 c	aromatic

integration ratio singlet (1.7):singlet (2.1) = 3:1

High resolution mass spectrum

molecular ion 428.1785 $C_{31}H_{24}O_2$

The structure, (18; n = 1), is consistent with these results.

m-ATB dimer

H'nmr spectrum

singlet	d 1.7	BPA methyl
singlet	d 2.1	ethynyl
tr dbl	d 6.7	aromatic meta subst.
multiplet	d 7.1 c	aromatic

integration ratio singlet (1.7):singlet (2.1) = 6.1

High resolution mass spectrum

unsatisfactory spectrum

The structure (18; n = 2), is consistent with these results.

Diethynylphenyl ether

H'nmr spectrum

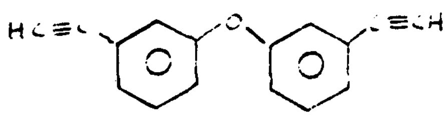
singlet	d 2.1	ethynyl
multiplet	d 7.1 c	aromatic

integration ratio singlet:mutilplet = 1:4

High resolution mass spectrum

molecular ion 218.0729 $C_{16}H_{10}O$

The structure (20) given below is consistent with these results.



20

(2) p-Ethynyl products

p-ATB monomer

H'nmr spectrum

singlet	d 1.68	BPA methyl
singlet	d 2.1	ethynyl
multiplet	d 7.1	aromatic

integration ratio singlet (1.68):singlet (2.1) = 3.1

High resolution mass spectrum

molecular ion 428.1788 $C_{31}H_{24}O_2$

The structure, (19; n = 1), is consistent with these results.

p-ATB dumer

H'nmr spectrum

singlet	d 1.68	BPA methyl
singlet	d 2.1	ethynyl
multiplet	d 7.1 c	aromatic

integration ratio singlet (1.68):singlet (2.1) = 6:1

High resolution mass spectrum

unsatisfactory spectrum

The structure, (19; n = 2), is consistent with the nmr spectrum.

By-product

H'nmr spectrum

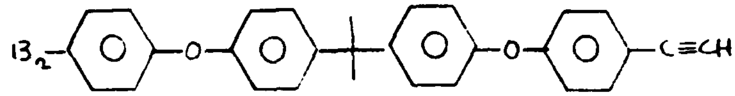
singlet	d 1.68	BPA methyl
singlet	d 2.1	ethynyl
multiplet	d 7.1 c	aromatic

integration ratio singlet (1.68):singlet (2.1) = 6:1

High resolution mass spectrum

molecular ion 483.0912 $C_{29}H_{23}BrO_2$

The product must be monobromo and monoethynyl terminated and the structure (21) given below is consistent with these results.



21

3. Scale-up of the Syntheses

a. Background:

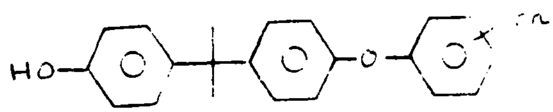
Monomer and oligomer mixtures of both bis-(4,4'-(3-ethynylphenoxy)phenyl)dimethylmethane (18) and bis-(4,4'-)4-ethynylphenoxy)-phenyl)dimethylmethane (19) have been synthesized at WPAFB. Three steps are required for each synthesis. Treatment of the appropriate dibromobenzene (meta- or para-) with bisphenol-A in collidine with cuprous oxide at 170°C gave m-BTB (8) or p-BTB (9). Treatment of (8) or (9) with 2-methyl-3-butyn-1-ol in triethylamine and pyridine solution in the presence of bis-triphenylphosphine palladium chloride, cuprous iodide and triphenylphosphine gave the diol (10) [or (11)]. Clevage of the hydroxypentyne moiety of (10) [or (11)] with potasium hydroxide then furnished the final products m-ATB (18) or p-ATB (19).

The monomer to oligomer ratio of the final acetylene terminated products is decided at the Ullman condensation stage. After consultation with WPAFB it was decided that the required products would best be made by using mole ratios of 6:10:1 of collidine:m-dibromobenzene:bisphenol-A to make m-BTB and mole ratios of 6:2:1 of collidine:p-dibromobenzene:bisphenol-A to make p-BTB. These ratios of reactants were chosen to give monomer to oligomer ratios of 75:25 for m-BTB and 55:45 for p-BTB.

b. Bromo terminated products:

(1) m-Bromo terminated mixtures (m-BTB)

The Ullman ether synthesis of m-BTB has been carried out at scales ranging from 0.05 to 2.0 g mole of bisphenol-A. Mole ratios of collidine:m-dibromobenzene:bisphenol-A:cuprous oxide of 6:10:1:2 were used and the reaction temperature was 170°C. A Dean and Stark trap was used to remove the traces of water formed in the reaction and the reaction was generally complete in 24 hours. Reactions were monitored by thin layer chromatography (tlc) using silica gel and a 2:8 mixture of acetone-toluene as eluant. The reaction was continued until the bisphenol-A and the half ether (22) had disappeared. After completion of the reaction, the reaction mixture was cooled and diluted with toluene. The solids were filtered off and washed with toluene until no more product could be detected in the filtrate. The toluene and excess m-dibromobenzene were removed by distillation under reduced pressure to give the product as a dark brown oil. Throughout the scale-up reactions the product composition was consistent at 75% monomer 25% oligomer and the yields were high at 90 - 95%.



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(2) p-Bromo terminated mixtures (p-BTB)

Ullman ether syntheses of p-BTB has been carried out at scales ranging from 0.03 to 2.0 g.mole of bisphenol-A. Mole ratios of 6:2:1:2 of collidine:p-dibromobenzene:bisphenol-A:cuprous oxide were used and a Dean and Stark trap was used in all the experiments to keep the reaction mixture anhydrous. The reactions proceeded smoothly and the bromophenyl ether (16) formation was successfully repressed. The reaction times varied from 48 to 72 hours; much longer than was required for the m-BTB. The progress of the reactions were monitored by tlc to ensure that the reaction was indeed complete. This was essential because if any unreacted half ether (22) remained it could not be removed from the reaction products except by chromatography which was impractical at the larger scales.

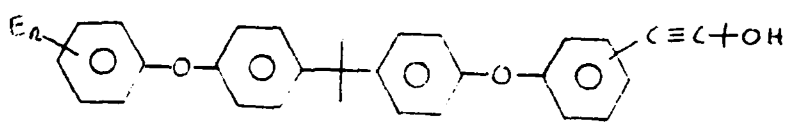
As these reactions were carried out with a 2:1 mole ratio of dibromobenzene to bisphenol-A some monobromo-BTB was to be expected in the product. Thin layer chromatography (silica, 3:7 toluene:hexane) showed the by-products as satellite spots with slightly lower Rf values than the major components.

c. Hydroxyisopentynyl terminated products:

(1) m-Hydroxyisopentynyl terminated mixtures (m-HBTB)

m-HTB was prepared at scales from 10 g to 500 g of product by reacting m-BTB with 2-methyl-3-butyn-2-ol in a solution of triethylamine and pyridine in the presence of bis-triphenylphosphine palladium and cuprous oxide. The reaction was normally complete in 24 hours as determined by tlc. The smaller scale reactions were worked up to give the m-HTB as a mixture of monomer and polymer in approximately the same ratio as was present in the m-BTB from which it was made. In larger scale reactions, the washed toluene extract of the m-HTB was treated directly with potassium hydroxide to afford m-ATB without isolating the m-HTB.

The reactions were monitored by tlc (silica, 2:8 acetone: toluene). Incomplete reaction was shown by the presence of two sets of spots with the m-bromoalcohol intermediate (23) at higher Rf values (0.5 - 0.8) and the desired m-HTB (10) at lower Rf values (0.3 - 0.5).



23

(2) p-Hydroxyisopentynyl terminated mixtures (p-HTB)

Para-HTB (11) was made in a similar way to m-HTB exce twice the amount of catalyst was necessary and even with thi catalyst the reaction times were longer (48 - 72 hours). The severe reaction conditions did not change the monomer to oligome nor did they produce greater amounts of side products.

d. Ethynyl terminated products:

(1) m-Ethynyl terminated mixtures (m-ATB)

Meta-ATB (12) was synthesized 10 to 500 g lots by hyd of m-HTB. The yield of m-ATB obtained was 65 to 75% based on th used in the preparation of the m-HTB. The reaction was carried heating a toluene solution of m-HTB with powdered potassium hy and continuously distilling off the acetone produced. Reactio normally complete in 6 to 8 hours and were worked up simply by with water until neutral and then evaporating to give the m-AT brown oil. Emulsification was a problem in the washing an extraction procedure but increasing the amount of toluene used the losses of product in the emulsions. The product was consi 70 - 75% monomer and 30 - 25% oligomer.

The 1 lb. sample was prepared in a single batch. Ini a sample of the product was analyzed and found to contain concentrations of palladium (14 ppm) and copper (30 ppm) as w traces of silica, calcium and barium than expected. Although levels were below the provisional specification levels, the prod retreated by dissolving it in toluene and washing the solutio aqueous diethylamine and then with water. The product was recov evaporating the washed solution.

(2) p-Ethynyl terminated mixtures (p-ATB)

Para-ATB (13) was made similarly at scales up to 40(product. There was no apparent difference in the reactivities meta- and para-products at this stage of the synthesis. The p-A consistently 55% monomer and 45% oligomer. Analysis of a small run sample (50 g p-ATB) showed a satisfactory level of pallad ppm) and copper (3 ppm). Analysis of the 1 lb sample has no performed.

(3) Conclusions

The processes for the preparation of bis-(4,4'-(3-ethynylphenoxy)phenyl)dimethylmethane (m-ATB) and bis-(4,4'-)4-ethynylphenoxy) phenyl)dimethylmethane (p-ATB) are satisfactory for scale-up to small scale (180 l. GLMS reactor) manufacture.

The processes use high cost raw materials, m- or p-dibromobenzene, collidine and a palladium catalyst but the excess didbromobenzene and the collidine can be recovered and reused.

Solvent costs and toxicity hazards have been reduced by replacing carbon tetrachloride and benzene by toluene. The use of toluene removed the need for drying agents as water can readily be removed azeotropically. The toluene can be recovered and reused.

It is not necessary to purify the raw materials, commercially available grades were used successfully.

The intermediate bromo- and hydroxyisopentynyl terminated products were purified simply by washing their solutions in toluene with the appropriate aqueous solutions. Isolation is not required.

SECTION III

EXPERIMENTAL

1. Methods and Materials

High resolution mass spectra were recorded on an AEI MS50 mass spectrometer coupled to a DS 50 computer. H'nmr spectra were recorded on a Varian HA100 spectrometer with TMS as an internal standard. Both mass spectra and H'nmr spectra were performed at the Chemistry Department of the University of Alberta under a regular service agreement.

Hplc analyses were determined on a Waters 6000A unit with a variable wavelength uv detector using 28% aqueous tetrahydrofuran as the mobile phase.

m-Dibromobenzene was purchased from Diaz Chemicals and was found to have a purity of 95.3%. p-Dibromobenzene, cuprous oxide, triphenylphosphine palladium chloride, 2-methyl-3-butyn-1-ol, triethylamine, and pyridine were purchased from Aldrich Chemicals. Technical grade toluene was used.

2. Synthesis of bis-4,4'-(3-bromophenoxy)phenyl)dimethyl methane (m-BTB)

To a 20 l. flask equipped with a Dean Stark trap, a reflux condenser, mechanical stirrer, N_2 inlet and thermometer was added 500 g (2.19 moles) of bisphenol-A, 6.27 kg (22 moles) of m-dibromobenzene, 1.6 kg (13.2 moles) of collidine and 800 g (5.6 moles) of cuprous oxide. The reaction mixture was stirred vigorously and heated at 170 - 172° until completion of reaction as determined by thin layer chromatography. To monitor the reaction, an aliquot of reaction mixture was diluted with toluene and acidified with conc. HCl. The toluene solution was then spotted on thin layer silica gel plates and eluted with 10% acetone in toluene. While the product appears at solvent front, the starting material bisphenol and the intermediate bromoalcohol appear at the origin and Rf = 0.6 respectively. The reaction was complete in 24 hours. The mixture was cooled in a water bath, diluted with 10 l. of toluene and filtered. The filter cake was washed thoroughly with toluene until the filtrate was free from product (tlc). The combined toluene filtrates were then washed with 3 l. of conc. HCl, 6 l. of 6N HCl and water repeatedly until neutral. Concentration of the toluene solution under reduced pressure then gave almost quantitative yield of m-BTB consisting of 75 - 77% monomer and 25 - 23% polymer.

3. Synthesis of bis-(4,4'-(3-(3-hydroxy-3-methylbutynylphenoxy)-phenyldimethylmethane (m-HTB)

To a 20 l. flask equipped with a reflux condenser, mechanical stirrer and N_2 inlet was added 600 g of m-BTB, 16.81 g (0.024 mole) of triphenylphosphine palladium dichloride, 14.5 g (0.076 mole) of cuprous iodide, 31.o g (0.12 mole) of triphenyl phosphine, 600 g (7.13 moles) of 2-methyl-3-butyn-2-ol, 2.5 l. of pyridine and 4.8 l. of pyridine. The reaction mixture was stirred vigorously and heated at reflux until reaction was complete as shown by thin layer chromatography. An aliquot of reaction was diluted with toluene and acidified with conc. HCl. Toluene solution was then spotted on thin layer silica gel plate and eluted with 20% acetone in toluene. While the starting material m-BTB appeared at solvent front, the desired m-HTB and the intermediate appeared at Rf = 0.4 and 0.6 respectively. At the end of reaction the reaction mixture was cooled in water bath and diluted with 10 l. of toluene and filtered. The filter cake was washed thoroughly with toluene until tlc showed absence of product in filtrate. The combined filtrates were then washed with 3 l. of 20% H_2SO_4, 4 l. of 6N HCl (3 times) and 5 l. of water. Finally, the toluene solution was heated at 60° with 6 l. of ethylenediamine (2 times), cooled and washed with water repeatedly until neutral. The toluene solution was distilled until free of water and used for subsequent conversion to m-ATB.

4. Synthesis of bis-(4,4'-(3-ethynylphenoxy)phenyl)dimethylmethane (m-ATB)

To the toluene solution containing m-HTB prepared previously, was added 410 g of powdered KOH. The reaction mixture was stirred vigorously and distilled until completion of reaction as determined by tlc on silica gel using 20% acetone in toluene as eluant. After completion of reaction (6 - 8 hr) the toluene solution was washed repeatedly with water until neutral. Concentration of toluene solution then furnished 340 g of p-ATB.

5. Synthesis of bis-(4,4'-(4-bromophenoxy)phenyl)dimethylmethane (p-BTB)

To a 10 l. flask equipped with a Dean-stark trap, reflux condenser, mechanical stirrer, N_2 inlet and thermometer was added 500 g (219 moles) of bisphenol-A, 1225 g (4.31 moles) of para-dibromobenzene, 1597 g (13.2 moles) of collidine and 786 g (5.5 moles) of cuprous oxide. The reaction mixture was stirred vigorously and heated at 170 - 172° until completion of reaction as determined by thin layer chromatographjy (see m-BTB). At the end of reaction, the mixture was cooled in a water bath and 6 l. of toluene was added to the reaction mixture. The precipitated salts were filtered and the filter cake washed thoroughly with toluene (5 - 6 l. approximately). The combined toluene filtrates were then washed with 3 l. of conc. HCl, 5 l. of 6N HCl and finally water until the water wash was neutral. The toluene solution was distilled under reduced pressure to give a quantative yield of p-BTB as a dark brown viscous oil. This consisted of approximately 55% monomer and 45% polymer.

6. Synthesis of bis-4,4'-(4-(3-hydroxy-3-methylbutynyl)phenoxy)-phenyl)dimethylmethane (p-HTB)

To a 10 l. flask equipped with a reflux condenser, mechanical stirrer and N_2 inlet was charged 600 g of p-BTB, 3 l. of triethylamine, 1.5 l. of pyridine, 9.6 g (0.014 mole) of bis-triphenylphosphine palladium dichloride, 8.4 g (0.044 mole) of cuprous iodide, 18 g (0.069 mole) of triphenylphosphine and 600 g (7.13 moles) of 2-methyl-3-butyn-2-ol. The reaction mixture was stirred at reflux until completion of reaction as determined by thin layer chromatography. To monitor the progress of reaction, an aliquot of reaction mixture was diluted with toluene and acidified with conc. HCl. Toluene solution was then spotted on thin layer silica gel plate and eluted with 20% acetone in toluene, in which starting material p-BTB appeared at the solvent front, the intermediate appeared at Rf=0.6 and desired diol at Rf=0.4.

At the end of reaction the mixture was cooled in water bath and diluted with 8 l. of toluene. The precipitated salts were filtered and washed thoroughly with toluene until tlc showed the absence of product in the filtrate. The combined filtrates were washed successively with 3 l. of 20% H_2SO_4, 4 l. of 6N HCl (2 times) and 5 l. of water. The toluene solution was then heated at 60° with 6 l. of ethylene diamine (2 times), cooled and washed with water until water wash was neutral. The toluene solution was distilled until free of water, and used in the subsequent acetone cleavage reaction.

7. Synthesis of bis-(4,4'-(4-ethynylphenoxy)phenyl)dimethylmethane

To the toluene solution containing p-HTB prepared previously was added 410 g of powdered potassium hydroxide. The reaction mixture was stirred vigorously and distilled until completion of reaction as determined by thin layer chromatography on silica gel using 20% acetone in toluene as eluant. The reaction was generally complete in 6 - 8 hours. After completion of reaction the toluene solution was washed with water repeatedly until water wash was neutral. Concentration of the toluene then afforded 320 g of p-ATB.

SECTION IV

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TABLE 1

The effect of a change in the mole ratio of the collidine on the monomer to oligomer ratio of m-BTB.

Collidine	m-DBB	BPA	% Yield	RC Time	monomer/oligomer
10	10	1	85	24	62/38
6	10	1	95	24	77/23
3	10	1	92	24	73/27

TABLE 2

The effect of a change in the mole ratio of the m-dibromobenzene on the monomer to oligomer ratio of m-BTB.

Collidine	m-DBB	BPA	% Yield	Rx Time	monomer/oligomer
10	10	1	85	24	62/38
10	3	1	67	36	30/70
10	2	1	75	36	20/80

TABLE 3

The effect of a change of the mole ratio of the p-dibromobenzene on the monomer to oligomer ratio of p-BTB.

Collidine	m-DBB	BPA	% Yield	Rx Time	monomer/oligomer
6	4	1	95	48-72	67/23
6	3	1	98	48-72	60/40
6	2	1	95-100	48-72	55/45

TABLE 4

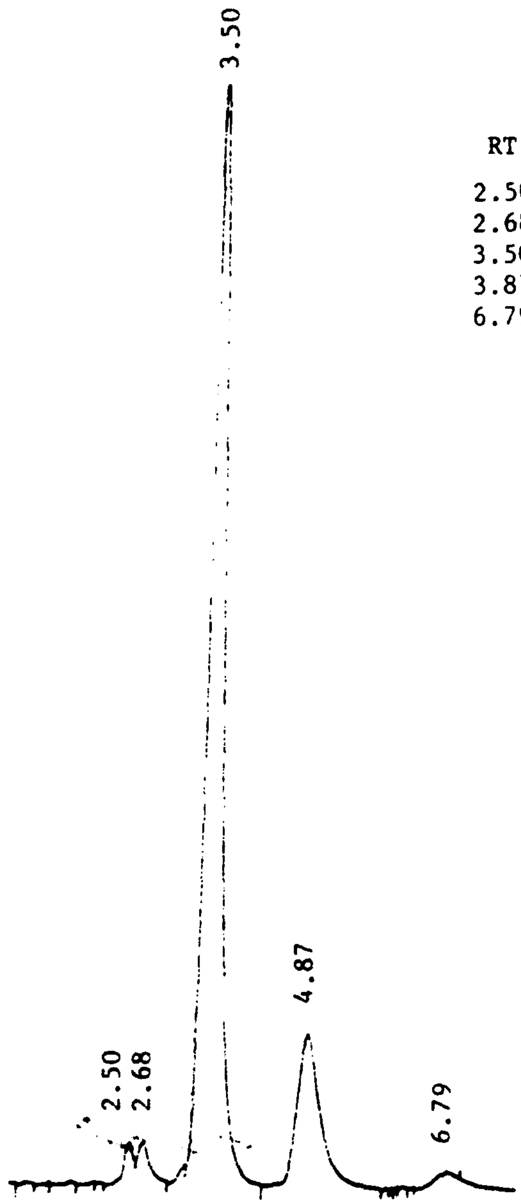
Comparison of the monomer to oligomer ratio estimated by the column chromatography and hplc methods.

m-BTB sample = 3.0 g

	% W	HPLC
Fraction 1 (0.027 g)	approx. 1%	3%
Fraction 2 (2.219 g) monomer	77.3%	76%
Fraction 3 (0.606 g) polymer	21.2%	21%

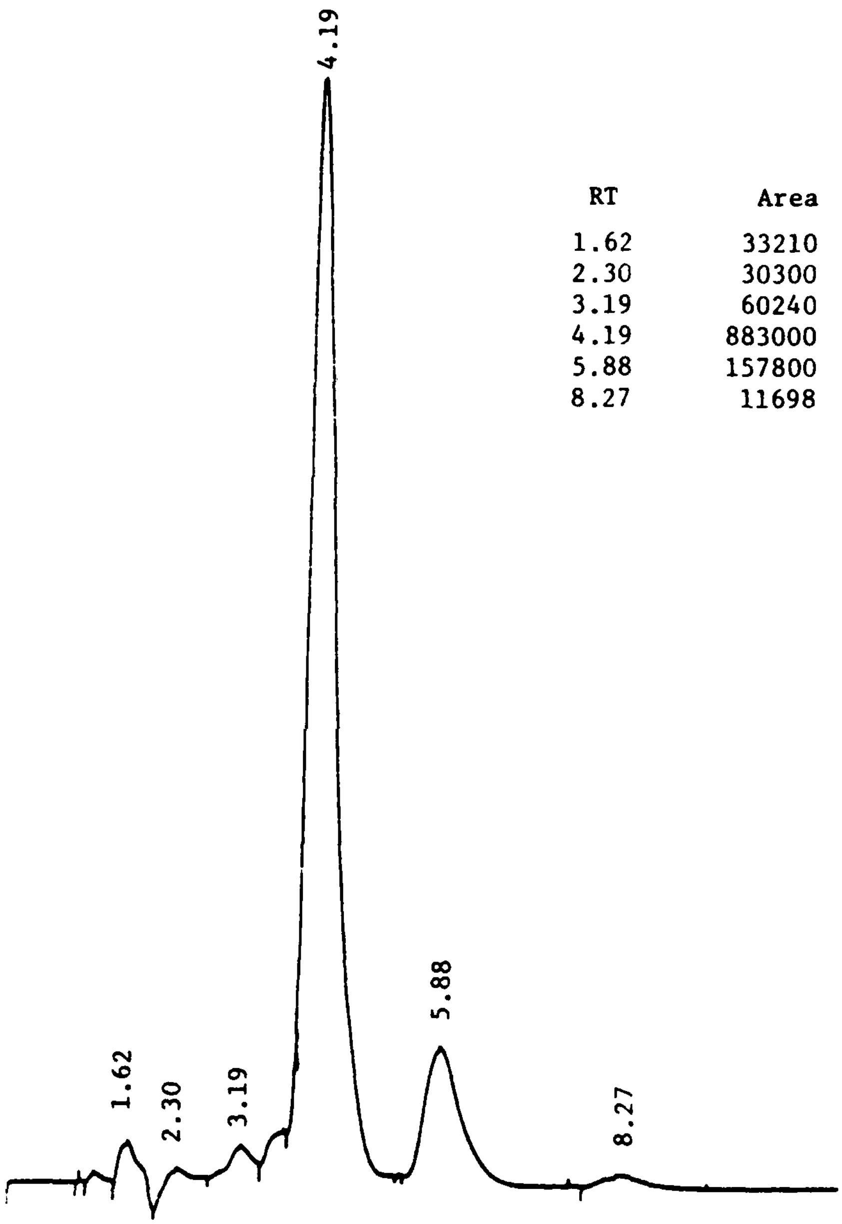
p-BTB sample = 3.0 g

	% W	HPLC
Fraction 1 (0.132 g)	4.4%	4.5%
Fraction 2 (1.612 g) monomer	54.2%	52.8%
Fraction 3 (1.225 g) polymer	41.2%	42.6%



RT	Area	Area %
2.50	11980	1.962
2.68	15220	2.493
3.50	470600	77.084
3.87	101300	16.593
6.79	4240	0.695

Figure 1: Typical hplc of m-BTB



RT	Area	Area %
1.62	33210	2.724
2.30	30300	2.485
3.19	60240	4.941
4.19	883000	72.428
5.88	157800	12.944
8.27	11698	8.959

Figure 2: Typical hplc of m-ATB

RT	Area	Area %
2.76	145800	4.550
3.17	38480	1.201
3.71	83320	2.600
4.12	1783000	55.647
5.79	764200	23.851
8.13	239800	7.484
11.39	60920	1.901

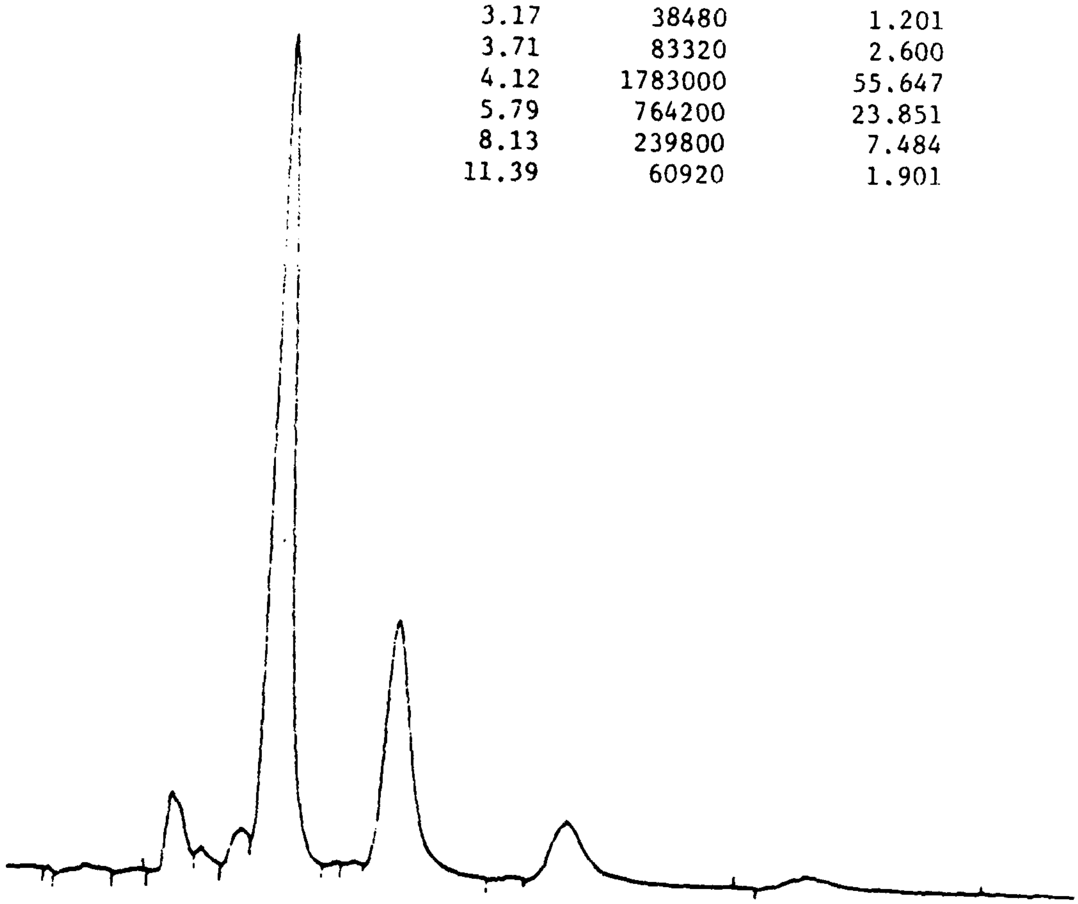
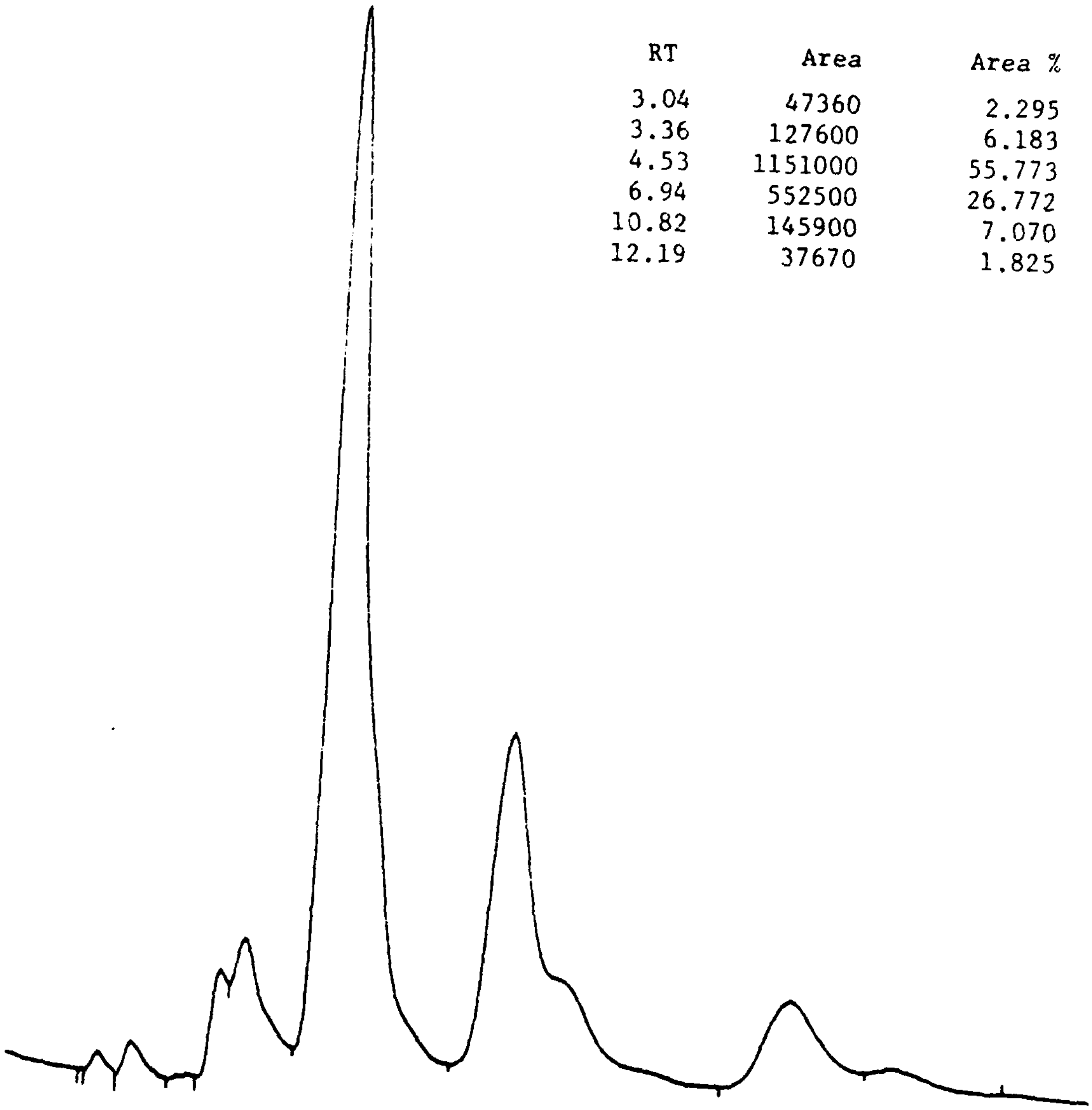


Figure 3: Typical hplc of p-BTB



RT	Area	Area %
3.04	47360	2.295
3.36	127600	6.183
4.53	1151000	55.773
6.94	552500	26.772
10.82	145900	7.070
12.19	37670	1.825

Figure 4: Typical hplc of p-ATB

Figure 5: H' nmr spectrum (aromatic region) of m-BTB monomer.

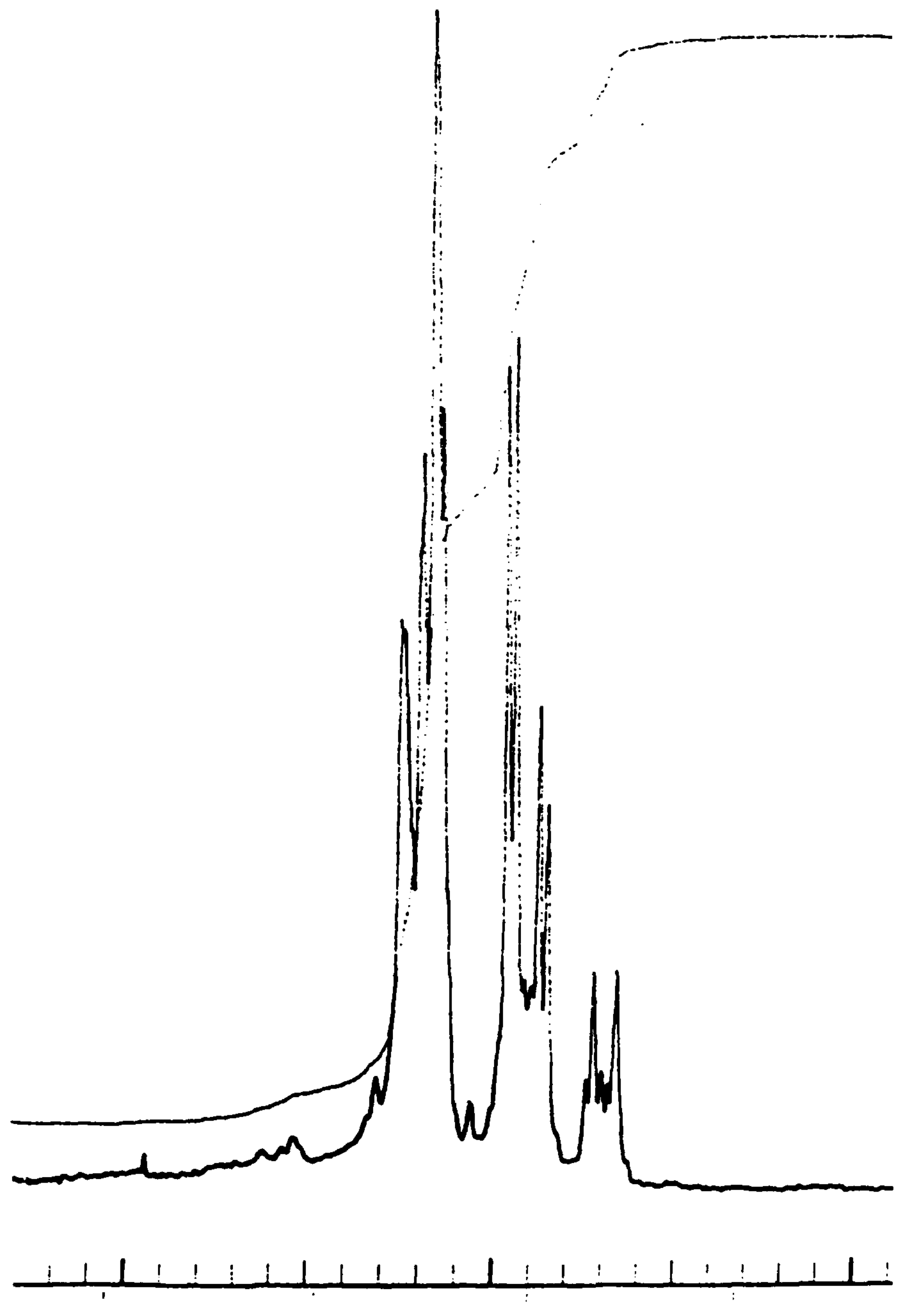


Figure 6: H' nmr spectrum (aromatic region) of m-BTB dimer.

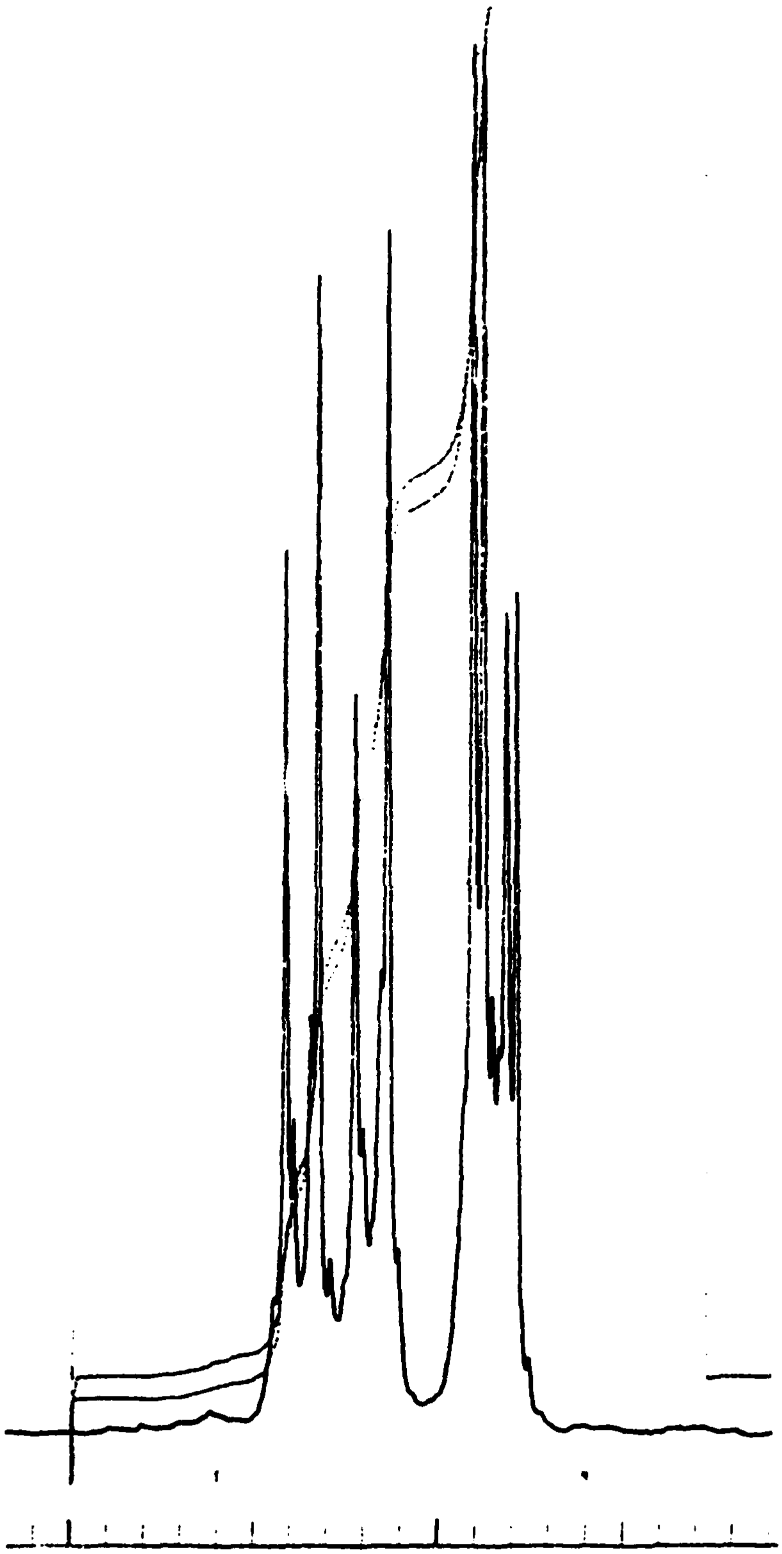


Figure 7: H' nmr spectrum (aromatic region) of p-BTB m^nomer

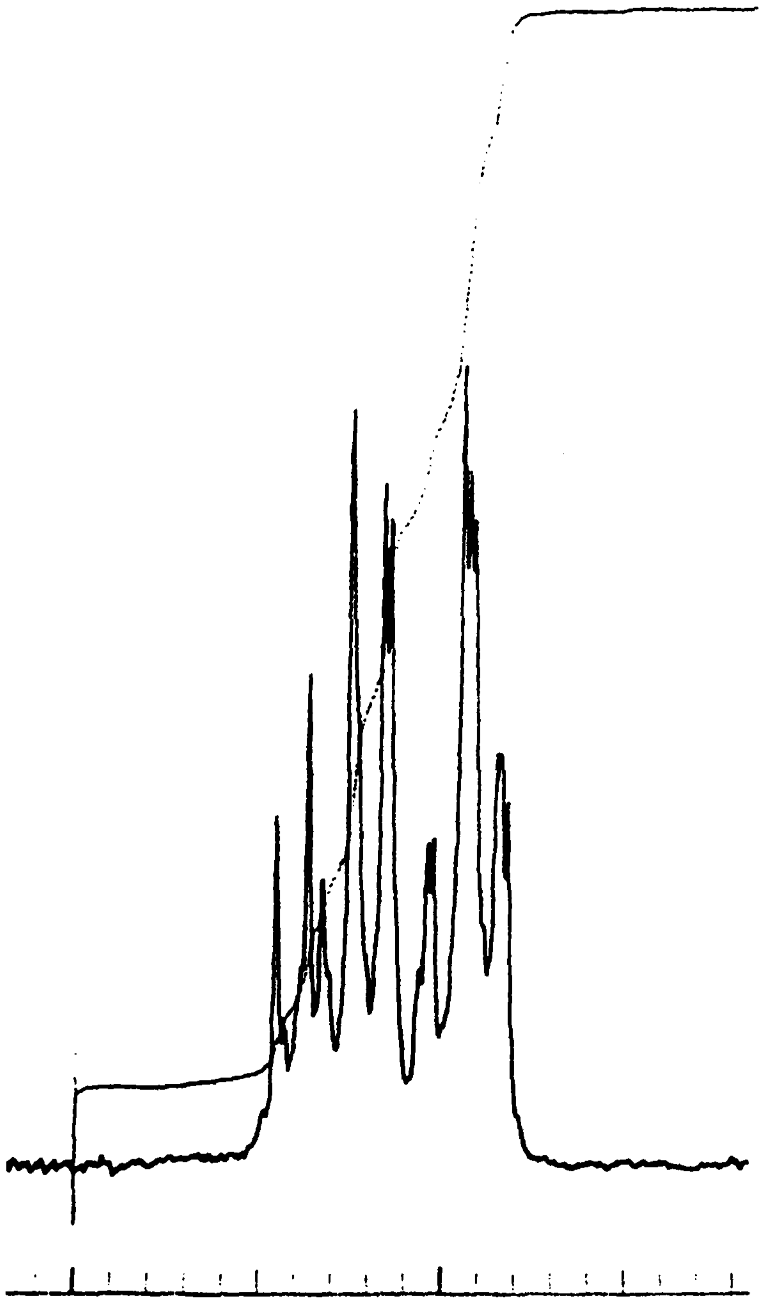


Figure 8: H'nmr spectrum (aromatic region) p-monobromo BTB monomer.

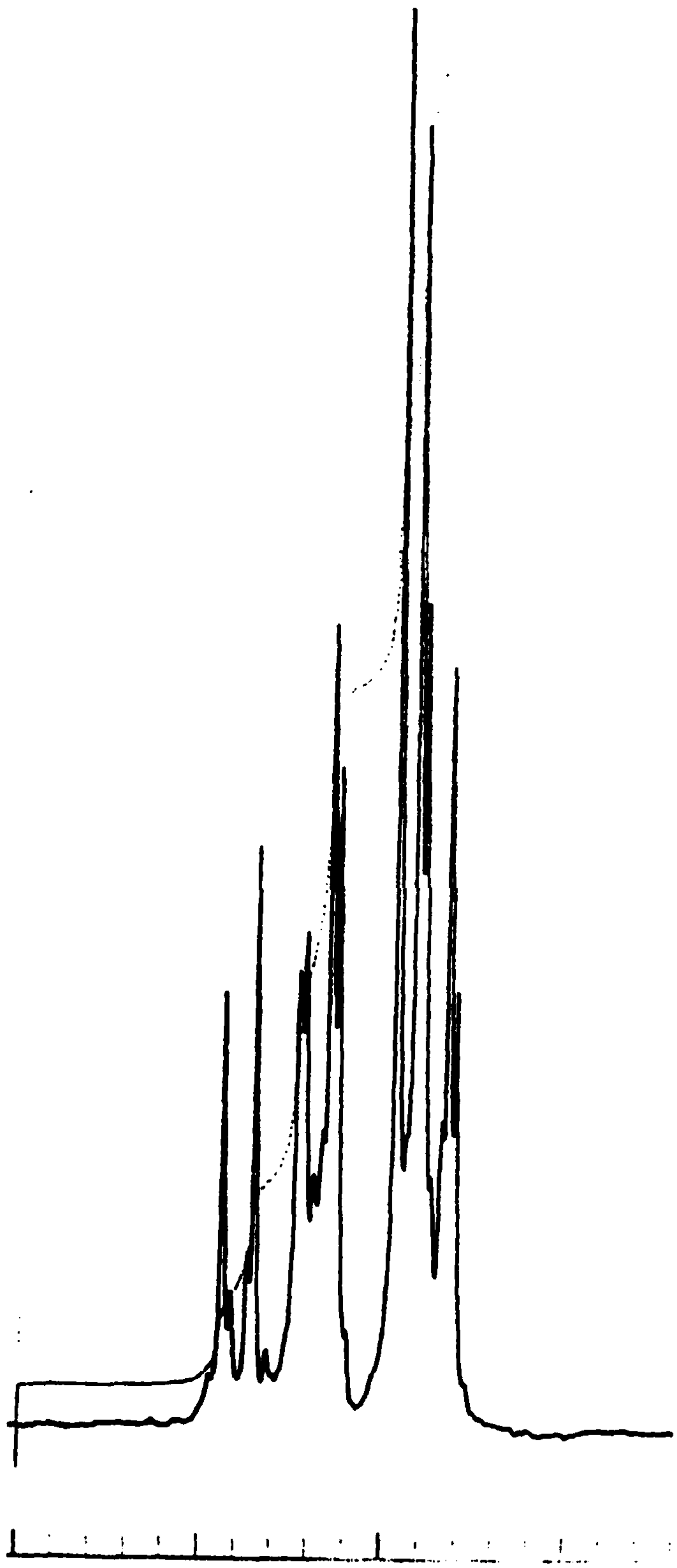


Figure 9: 'l'nmr spectrum (aromatic region) of p-BT? dimer.

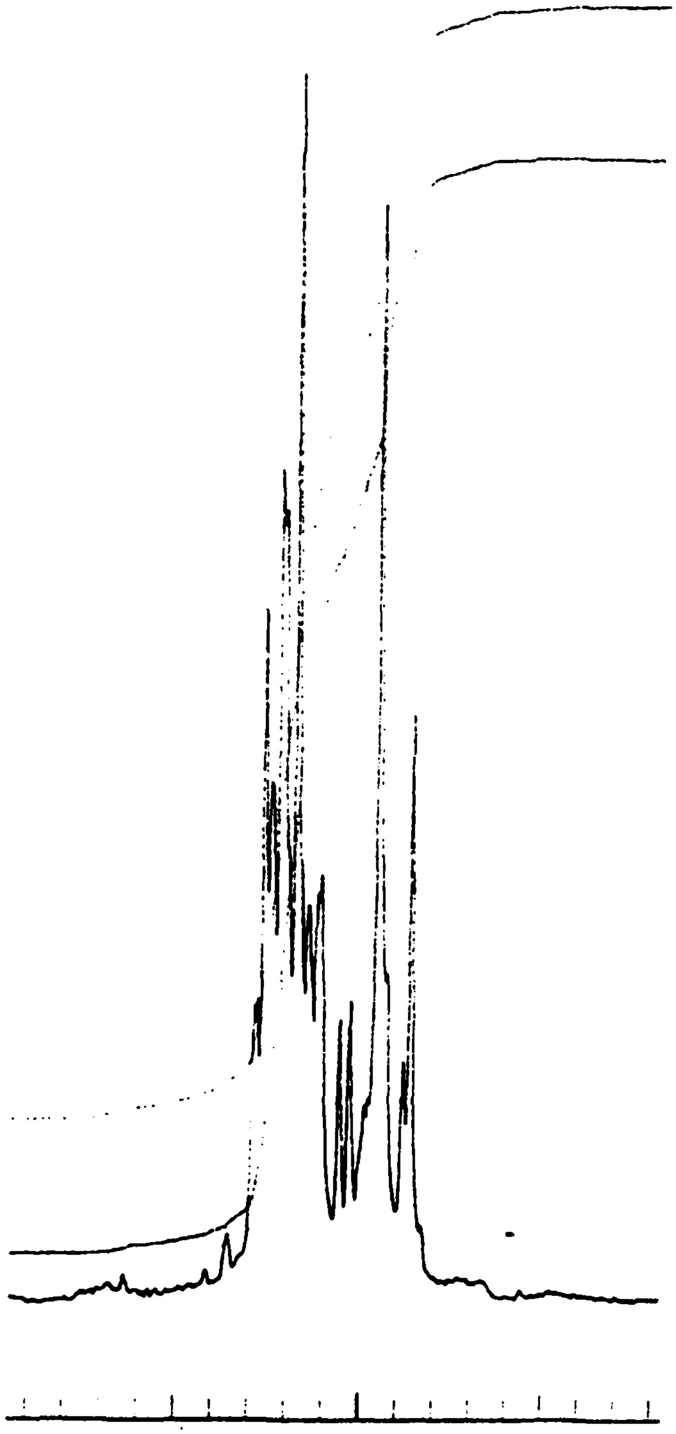


Figure 10: H'nmr spectrum (aromatic region) of m-ATB monomer.

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